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(71) Applicant: TOYOTA JIDOSHA KABUSHIKI KAISHA
1, Toyota-cho Toyota-shi
Aichi-ken 471(JP)

(72) Inventor: TAKAHASHI, Yoshinobu
48 Heiwacho 4-chome
Toyota-shi Aichi 471(JP)

(72) Inventor: YOKOI, Masanori
3934-17, Harukishimizu Tougoucho
Aishi-gun Aichi 470-01(JP)

(72) Inventor: MORI, Takanobu
530, Toyotacho Toyota-shi
Aichi 471(JP)

(72) Inventor: ODANAKA, Masamitsu
20-36, Hisaokacho 5-chome
Toyota-shi Aichi 471(JP)

(72) Inventor: MURASE, Haruo
51, Maruyamacho 7-chome
Toyota-shi Aichi 471(JP)

(72) Inventor: KOJIMA, Masayuki
16, Seishincho 1-chome
Toyota-shi Aichi 471(JP)

(74) Representative: Hirsch, Marc-Roger
34 rue de Bassano
F-75008 Paris(FR)

(64) ELECTRODE FOR USE IN CATIONIC ELECTRODEPOSITION COATING AND COATING METHOD USING THE SAME.

(67) An electrode for use in cationic electrodeposition coating comprising a sintered metal oxide having electroconductivity such as ferrite or magnetite, and a method for cationic electrodeposition coating using said electrode as an anode.

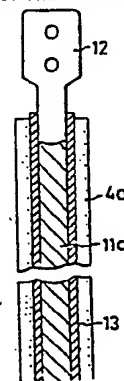


Fig. 4

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ELECTRODE FOR CATIONIC ELECTRO DEPOSITION
COATING AND METHOD FOR COATING BY USE OF THE ELECTRODE

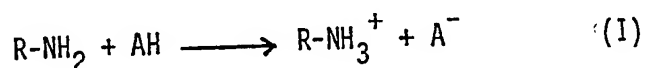
This invention relates to an electrode formed of a sintered mass of a metal oxide to be used for coating by cationic electrodeposition and to a method for electrodeposition coating by use of the electrode mentioned above.

In recent years , increasing importance has come to be attached to the improvement in anti-corrosion in the case of coating automobile bodies. The measures for anti-corrosion have been studied in terms of base materials, chemical treatments, types of paints, manners of paint application, automobile body designs, etc. from various angles. Among others, the technique of electrodeposition coating constitutes the most effective and economic method for rendering anti-corrosive the inner surfaces of complicated and hollow structures such as automobile bodies, for example, and even those portions which do not readily permit spray coating. Thus, the electrodeposition coating is extensively used today.

The conventional method for electrodeposition coating has preponderantly used anionic electrodepositing paints in consideration of the low cost of paints so used, the relatively low temperature for baking paints, and the relatively low cost of equipment involved. In accordance with the method for anionic electrodeposition coating, however, the article subjected to coating which is used as an anode is dissolved out in the

course of electrodeposition coating, whereas the cathode such as of iron immersed in the electrodepositing cell or paint is not dissolved out. Consequently, the effect of the chemically formed coat is degraded and the thickness of the coat formed on the surface of the article to be coated under treatment is small. Accordingly, with the progressive aggravation of the corrosive environment, it has been proved that the conventional anionic electrodeposition coating is not necessarily satisfactory. For this reason, the technique of cationic electrodeposition coating has recently come to find increasing acceptance.

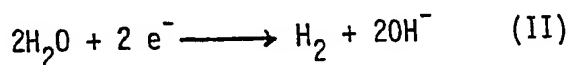
To effect the cationic electrodeposition coating, a water-insoluble polyamine resin, $R-NH_2$ is obtained by adding a primary amine or secondary amine to the glycidyl group of a water-insoluble resin such as, for example, a bisphenol type epoxy resin thereby effecting ring cleavage thereof, and then an organic acid such as acetic acid or lactic acid is caused to react, as a neutralizing agent (water-solubilizing agent) AH , with the aforementioned water-insoluble polyamine resin to produce an aqueous-resin, $R-NH_3^+$, as shown by the following reaction formula (I)



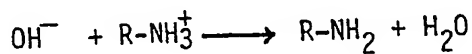
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In a cationic electrodepositing paint solution formed of the aforementioned water-soluble resin, and if necessary, a crosslinking agent and a pigment, an article to be coated is immersed as a negatively charged electrode (hereinafter referred to as "cathode"). Separately a positively charged electrode (hereinafter referred to as "anode") such as of stainless steel or carbon is immersed in the same solution. Electric current is passed between the cathode (the article under treatment) and the anode.

By the passage of the electric current, the positively charged paint components electrophoretically migrate in the solution and, on arrival at the article (the cathode) coagulates and precipitates by emitting the electric charges as shown by the following formula (II) and gives rise to a water-insoluble coat on the article.

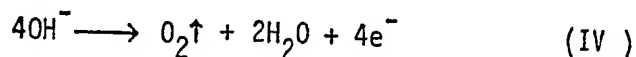


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On the anode which is made of a metal such as, for example, stainless steel as indicated in the formula (III), dissolution of metal ions and simultaneous generation of oxygen shown by the formula (IV) are observed



In case the anode is made of carbon, since it is not a metal, the dissolution indicated by the formula (III) does not occur, but the generation of oxygen through the reaction of the formula (IV) does occur. Consequently, the carbon of the anode itself is oxidized. Therefore, with the lapse of time, the anode loses its weight and eventually a flaw is developed.

Particularly in the case of an anode made of a metal, the metal ions dissolved out from the anode get mixed into the solution. When the paint component is coagulated and precipitated, these metal ions are simultaneously coagulated and precipitated to the article. The coat which is consequently obtained suffers from poor anti-corrosion property or coarse coating surface. In the case of an anode made of carbon, the oxidation causes the anode to shed fine carbon particles into the solution. If the electrodeposition coating is continued with carbon particles contained in the solution, gritty prominences stand out on the surface of the coated article, with the result that the produced coat suffers from inferior appearance and deficient anti-corrosion property.

As materials for the anode which avoid release of metal ions, the use of high-grade stainless steel of SUS-316 or the like, or a noble metal such as platinum may be considered. Stainless steel, in addition to being expensive, is inevitably susceptible to release of metal ions, if only to a slight extent. The noble metal is too expensive to be feasible for the use contemplated. Carbon and graphite have a problem that they have poor processibility.

This invention is directed to solving the aforementioned problems suffered by the prior art and is aimed at the adoption, as a material for the anode, of a sintered mass of a metal oxide which is indissolvable or sparingly dissolvable and is an electric conductor. It is also aimed at disclosing a specific construction of the anode using a sintered mass of a metal oxide having poor moldability and processibility.

A method for the cationic electrodeposition coating according to the present invention comprises the steps of placing an article subjected to coating in a paint solution, placing paired electrode as opposed to the article in the paint solution, and applying a DC voltage between the article and the paired electrode thereby forming on the surface of the article a coat of cationic electrodeposit, and is characterized by using, as the material for the paired electrode mentioned above, a sintered mass of electroconductive metal oxide.

The sintered mass of metal oxide which is used for the paired electrode, i.e. anode, in the present invention abounds with electroconductivity. Typical examples of the sintered mass are a magnetic iron oxide represented by $\text{FeO-Fe}_2\text{O}_3$ which is popularly called magnetite and a magnetic metal oxide represented by $\text{MO.nFe}_2\text{O}_3$ which is called ferrite. In the formula, M denotes a divalent metal ion such as of Mn, Ni, Cu, Mg, Co, or Zn.

Because of the intended purpose, the sintered metal mass to be used in this invention is required to possess electric conductivity.

In the case of the aforementioned magnetite, since the specific resistance is sufficiently low, the electric conductivity does not pose any serious problem. In the case of the ferrite, the specific resistance is fairly variable with the composition. Generally, ferrites possess ferromagnetism.

The ferrites of the type which are now used in the electronic industry as various transformers, permanent magnets, memory elements, and magnetic elements in televisions, radios, audio devices, and telecommunication devices possess varying specific resistance within a wide range of 100 Ωcm to 100 $\text{M}\Omega\text{cm}$. Among ferrites, some of those having large values of specific resistance may suffer from decline of current and evolution of heat and, consequently, prove to be unfit for use as anodes. The ferrite to be used as the material for the anode in the present invention is required to possess a low degree of specific resistance. In the ferrite, the electric conduction is preponderantly caused by the hopping of electrons between Fe^{2+} and Fe^{3+} . For making the ferrite possess a low degree of specific resistance, therefore, the composition of the ferrite must be excessively rich in Fe_2O_3 . The sintered mass of metal oxide to be used as the anode for the cationic electrodeposition coating according to the present invention is desirably such a composition that the value

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of the volume specific resistance, determined in accordance with the specification of ASTM D 257-61, is not more than $10^5 \Omega \text{ cm}$, preferably not more than $10^3 \Omega \text{ cm}$ and more preferably not more than $0.3 \Omega \text{ cm}$, at a temperature of 20°C and a load voltage of 20V. Specifically this is

5 a sintered mass of the metal oxide having a spinelcrystalline structure wherein iron oxide and metal oxides other than iron oxide (such as NiO , MnO , CoO , MgO , CuO , ZnO and CdO , for example) are combined in a specific mixing ratio, i.e., the sintered mass comprises iron oxide and metal oxides other than iron oxide, the metal oxide other than iron oxide
10 being 5-40 weight %, preferably 20-40 weight %, and most preferably 40% with respect to the total mole of the sintered mass.

In the case of a magnetic iron oxide, it is desired to be composed of 30 to 50% of FeO and 50 to 70% of Fe_2O_3 , preferably 35 to 45% of FeO and 65 to 55% of Fe_2O_3 . A sintered mass composed of 44.0% of FeO , 53.5%
15 of Fe_2O_3 , 1.0% of SiO_2 , 0.9% of Al_2O_3 , 0.5% of CaO and 0.1% of MgO is employed as one of most preferable metal oxide. In the case of magnetic iron oxide, it may include except FeO and Fe_2O_3 4 to 6% of SiO_2 , 0.1 to 1.0% of CaO , MgO and Al_2O_3 respectively.

The anti-corrosion property of the aforementioned magnetic iron
20 oxide and ferrite as an anode excels that of the conventional material for the anode such as stainless steel (SUS 304, SUS 316, SUS 317) or carbon like graphite. Particularly, the ferrite is desirable because it sparingly dissolves out.

The metal oxide electrodes are known and the manufacturing processes
25 thereof are also known, for instance, from Japanese Patent Publication Nos 30151/1977 and 35394/1976. The electrode according to the present invention can be therefore produced using the aforementioned magnetic iron oxide or ferrite in accordance with the conventional processes.

Illustrative of such producing processes is one in which 5 to 40
30 mol% of at least one of metal oxides of MO (M denotes Mn, Ni, Co, Mg, Cu, Zn, or Cd) is added to 95 to 60 mol% of Fe_2O_3 ; heating is carried out in the air at 800 to 1000°C for 1 to 3 hours after mixing in a ball mill; and the cooled mass is crushed to obtain fine powder. The fine powder is molded under pressure, or a muddy substance obtained by adding water to this
35 fine powder is cast-molded after pouring into a mold or by an appropriate method such as extrusion to obtain a desired shape of a molded product. The molded product thus obtained is sintered in an inert gas containing

less than 5 vol. % of O_2 , for instance, in the N_2 or CO_2 atmosphere at 1300 to 1400°C for 3 to 5 hours and then gradually cooled in an inert gas containing less volume of O_2 , such as N_2 or CO_2 atmosphere to obtain the intended electrode. The electrode thus obtained has a
5 relatively high mechanical strength and exhibits the specific resistance fallen within the above-mentioned range.

In the above, although Fe_2O_3 and MO (M being the same as given above) are employed as starting materials, instead of Fe_2O_3 , there may be employed at least one kind of Fe, FeO and Fe_2O_3 in such an amount
10 that the amount is 95 to 60% when calculated as Fe_2O_3 . Further, instead of the oxide such as MO , there may be employed a compound such as carbonate and oxalate which can produce their oxide upon heating.

The magnetite electrode can be obtained by a similar manner to that mentioned above. For instance, pure Fe_3O_4 as starting material together
15 with polyvinylalcohol as binder are granulated and then molded, followed by solid phase-sintering at an inert atmosphere such as CO_2 gas at 1200 to 1300°C to obtain the intended electrode.

The anode of the sintered mass of metal oxide only, according to the present invention, may be used in the shape of a flat plate, an
20 angular column, or a circular rod. For the purpose of giving a large surface area to the anode and avoiding the nonuniform current distribution originating in the electrode based on the volume specific resistance of the sintered mass of metal oxide itself possibly induced when a large amount of electric current flows and further for the purpose of avoiding
25 possible breakage of the anode such as due to mechanical impacts, the anode may be constituted such that the sintered mass of metal oxide is molded into a cylindrical tube with one end thereof closed and the cavity such a metal member as aluminum core, iron core, stainless steel core, copper core, or twisted strands of copper, particularly stainless steel
30 material is inserted into the cylindrical body through an electroconductive material such as lead, solder, or conductive resin (e.g., an epoxy resin containing silver or graphite, commercially available under trademark designation of "Dotite").

When stainless steel is employed as a core material in the above-
35 mentioned constructure, it is possible to preclude rise of temperature or ununiformity of current distribution when a large amount of electric current is flown. Owing to the characteristic property of stainless steel,

the metal ions will dissolve out only to a slight extent even when the sintered mass is broken.

When the article to be coated by electrodeposition has a large, complicated structure, and even the inner surface of the box-like structure is required to be thoroughly and uniformly coated as in the case of an automobile body, the electrodepositing tank itself becomes bulky and the anode to be used therein also becomes large. In case the installation of the anode only in the lateral portion of the electrodepositing cell fails to give an ample throwing power and sufficient thickness, it is found necessary to have another anode installed further on the bottom surface of the electrodepositing cell.

When the anode is desired to be given an increased size so as to overcome the problems just mentioned above, since it is difficult to produce a sufficiently large tube of the sintered mass of metal oxide, it is desirable to obtain a large anode by preparing a one end-closed tube and a tube with the both ends thereof closed, then preparing a bar-shaped metal member as a core material, inserting the core material in the two tubes, and joining the core material fast to the tubes through an electroconductive material. The joining between the two tubes is desirably effected by engaging a tube of rigid resin around the adjoining portions of the two tubes bridging them and integrating the rigid resin tube with the two tubes of sintered mass by means of rigid resin filled therebetween.

The electrode to be installed on the bottom surface of the electrodepositing cell may be obtained by joining a covered lead wire to a magnetite or ferrite electrode, positioning a tube of rigid resin around the electrode so as to cover a part of the outer circumference of the tube of sintered mass as well as a part of the lead wire, while the rigid resin tube being bridged between the joint filling the space between rigid resin tube and joint with a thermosetting resin and causing it to harden, and optionally having rings or caps of rigid resin screwed to the opposite ends of the rigid resin tube. When the electrode is constructed as described above, the core materials of the lead wire and the electrode are not attacked by the electrodepositing liquid in the electrodepositing cell. Consequently, the electrode may be easily set in an arbitrary position within the cell.

According to the present invention as above-mentioned the surface area of the electrode can be increased by forming the sintered metal oxide into a tubular shape. Further it is another advantage that the tube into

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which is inserted a core of such as copper or stainless steel can be strengthened.

In the case of the electrode which consists of a sintered metal oxide solely, the temperature around the electrode terminal will rise when a big current is flown and there happens to be an unequal current distribution from the electrode because of the electric resistance of the coating liquid and the specific volume resistance of the metal oxide itself, however in the present invention such a disadvantage won't happen because the electrode has metal core inserted in it. Still further according to the combined structure of the electrode of the present invention, it is advantageous to be able to make such a large size of the electrode as desired.

Further in the lead wire joined-structure electrode according to the present invention having a sheathed lead wire, the outer circumference of the sheathed lead wire is covered with metal oxide sintered mass to be in contact with the liquid; and the joint between the lead wires is covered with the resin. Therefore, an appropriate number of the electrodes can be arbitrarily and easily placed in a suitable location of the electrodeposition cell. Accordingly, it is possible to attain an excellent throwing power and a desired film thickness of the coating even in the case of coating a large size of a parts to be coated such as automobile body.

Brief Explanation of the Drawing :

- Figure 1 is a lateral cross section view illustrating a system for carrying out the method for cationic electrodeposition coating;
- Figure 2 is a lateral cross section view illustrating another system for carrying out the method for cationic electrodeposition coating.
- Figure 3 is a longitudinal cross section view of yet another system for carrying out the method for cationic electrodeposition coating;
- Figure 4 is a longitudinal cross section view illustrating an electrode of this invention using a metal member as a core material;
- Figure 5 is a lateral cross section view of the electrode in figure 4;
- Figure 6 and Figure 7 are cross section views illustrating an electrode of the present invention formed solely of a sintered mass of metal oxide;
- Figure 8 is a cross section view illustrating a electrode of this invention, wherein sintered masses of metal oxide are joined to

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each other;

- Figure 9 is a cross section view of the essential part of the electrode of figure 8;
- Figure 10 is a front view illustrating an electrode having a lead wire connected thereto;
- Figure 11 is a cross section view of the essential part of the electrode in figure 10;
- Figure 12 and Figure 13 are cross section views illustrating the electrode shown in Figure 10 as laid out for actual service.

Best mode of the invention:

Now, the present invention will be described below with reference to working examples and controls. The value of each volume specific resistance given in these examples and controls were those obtained by the measurement carried out at 20°C and 20V in accordance with the method of ASTM D 257-61.

EXAMPLE 1 :

(A) Preparation of anode plate

Anode plates having 160 mm in length, 50mm in width, and 4mm in thickness were prepared through sintering using as raw materials magnetic iron oxide and ferrites A through D having different values of volume specific resistance. The volume specific resistance values of the sintered masses (anode plates) thus obtained were as shown in Table 1-2.

Table 1-1

Component Electrode	Fe_2O_3	NiO	MnO
Ferrite A	53 mol%	30 mol%	17 mol%
Ferrite B	53 "	37 "	10 "
Ferrite C	55 "	45 "	0 "
Ferrite D	60 " "	40 "	0 "

Fine powder is produced by mixing at least one of NiO and MnO

together with Fe_2O_3 at the above-shown ratios of Table 1-1; well mixing them, for instance, in a ball mill; heating the mixture in the air at 800 to 1000°C for 1 to 3 hours; and crushing the mass thus obtained after cooling. A muddy substance obtained by adding water to the fine powder is extrusion-molded into a desired shape of a molded mass. Then, the molded mass is sintered at 1300 to 1400°C in the N_2 atmosphere containing less than 2 vol. % of O_2 for 3 to 5 hours and cooling is effected gradually in the N_2 gas containing less volume of O_2 to obtain the intended electrode.

(B) Electrodeposition Coating :

(1) Preparation of paint

Epoxy type polyamino resin having a resin base number 80 was neutralized at a neutralization equivalent 0.5 with acetic acid and dissolved in a deionized water containing ethylene glycol monoethyl ether acetate to produce varnish. The varnish thus prepared and 3 parts of carbon black and 6 parts of talc both based on 100 parts of the solid content of the varnish were subjected to dispersion in a mill for 20 hours to produce a cationic electrodepositing paint. The paint thus obtained was diluted with deionized water to a solid content of 12%

(2) Method of coating

As illustrated in Figure 1, a container which was obtained by providing a vinyl chloride resin lining 2 for a tank 1 of steel plate measuring 200mm in length, 110mm in width, and 150mm in depth was filled with the paint solution 3 prepared as described above. Then the sintered ferrite plates (paired electrodes) 4, 4 prepared as described in (A) above were fixed in the bath while their portions 10mm downward from their respective upper ends stood over from the surface of the bath, whereas an article 5 to be coated which is made of steel plate treated with zinc phosphate (a cold-rolled steel plate SPC of 150x50x0.8mm treated in advance with Bonderite # 137 made by Nihon Parkerizing Co, Ltd.) was immersed in the aforementioned bath. The two paired electrodes 4, 4 were disposed symmetrically about the article 5 under treatment so that a coat would be uniformly formed on the article 5. These paired electrodes 4,

4 were interconnected with a lead wire 6. Further, the article 5 was electrically connected via a contact 8 to a power supply 7 which in turn was connected to the aforementioned lead wire 6. With the bath kept in the state described above, electric current was passed under the following conditions. The paired electrodes 4, 4 were positively charged and used as anodes and the article 5 used as a cathode, with the result that the cationic paint was deposited on the surface of the article 5.

(Electrodeposition conditions)

o	Bath temperature	30°C
o	Distance between electrodes	150mm
o	Anode area	75cm ²
o	Cathode area	75cm ²
o	DC voltage	130V and 160V
o	Period of current flow	3minutes

After the electrodeposition coating, tap water at 20°C was sprayed under pressure of 0.5kg/cm² to wash the coated article for one minute. Then, the baking-curing was effected at 180°C for 30minutes. The electrodeposition coating was similarly conducted using the anodes produced from the different raw materials and the value of initial current and thickness of each coat were determined. The results were as shown in Table 1-2.

Control 1:

Similarly with the procedure of Example 1 (B), the electrodeposition coating was carried out by using carbon (graphite electrode made by Tokai Carbon Co., Ltd. and marketed under trademark "G 152") and stainless steel SUS 316 as materials for paired electrodes (anodes). With the use of the above anodes, the value of initial current at the electrodeposition and thickness of each coat were measured. The results were as shown in Table 1-2.

TABLE 1-2

Example		Example 1							Control 1
Voltage	Material anode	Magnetic iron oxide	ferrite A	ferrite B	ferrite C	Ferrite D	carbon	Stainless steem SUS 316	
130 V	Thickness of deposited coat (μ)	15	10	14	15	15	14	15	
	Value of initial current (A)	2.0	1.1	1.8	1.8	1.9	1.8	1.9	
160 V	Thickness of deposited coat (μ)	21	16	19	20	20	20	20	
	Value of initial current (A)	2.2	1.3	2.0	2.1	2.2	2.2	2.2	
Value of volume specific resistance ($\Omega \cdot \text{cm}$)		less than 1×10^{-1}	2×10^5	1×10^3	90	0.3	-	-	

EXAMPLE 2 :

(A) Preparation of anode plate

Similarly with the procedure of Example 1 (A), anode plates were made by using magnetic iron oxide and ferrite D.

(B) Method for test for anti-corrosiveness

A 5 wt.% solution of acetic acid diluted with deionized water and a 5 wt. % solution of lactic acid diluted with deionized water were mixed at a mixing ratio of 1:1. The resultant mixture was placed in the similar container with a resin lining to that used in Example 1 (B). In the bath, the paired anode plates prepared as described in (A) above were set in such a position that their portions 10mm downward from their respective upper ends stood out over the surface of the bath and a cold rolled SPC steel plate was set therein as a cathode. Electrolysis was carried out under the following conditions. The anode plates were tested for anticorrosiveness, by measuring the loss of weight of each anode. The amounts of dissolution thus measured were as shown in Table 2-1.

(Conditions of electrolysis)

- o Bath temperature 30°C
- o Distance between anodes 150mm
- o Area of anodes and cathodes 75cm²
- o DC current 5A/dm² and 0.01 A/dm² alternately used at intervals of 1 hour
- o Period 100 to 1000 hours

Control 2 :

The same carbon and stainless steel SUS 316 as involved in Control 1 were used as anode and the anodes were tested for anti-corrosiveness by following the procedure of Example 2 (B). The amounts of anodes dissolved out in the test were as shown in Table 2-1.

Table 2-1

Material of anode	Amount dissolved out (g/A year)
Magnetic iron oxide	50
Ferrite E	0,5
Stainless steel SUS 316	10.000
Carbon (graphite)	1.000

Similarly to the above test, there were measured the dissolved amounts and resistances of electrode of nickel-ferrite ($\text{Fe}_2\text{O}_3\text{-NiO}$) in which the mol% of NiO is varied in the range of 5 to 45 mol%, the results being shown in Table 2-2.

5 The electrodes in this test were produced similarly in Example 1.

Table 2-2

10		NiO(mol%)	Dissolved-out amount (g/A.year)	Resistance (Ωcm)
	Ferrite D	40	0.5	0.3
	Ni-ferrite I	30	1.0	0.07
	Ni-ferrite II	20	2.0	0.03
	Ni-ferrite III	10	4.5	0.02
15	Ni-ferrite IV	5	7.0	0.01
	Ni-ferrite V	2	12.0	0.005
	Ni-ferrite VI	43	0.3	3.0
	Ferrite C	45	below 0.1	90.0

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It is seen from Table 2-2 that 5-40 mol% of NiO is more excellent.

EXAMPLE 3.

In a field electrodeposition coating process, as illustrated in Figure 2, a container in which a lining 2 such as of vinyl chloride is provided on the inner surface of a tank 1 of steel plate was filled with a paint solution 3. This paint had substantially the same composition as described in Example 1 (B). In the paint solution 3, the anode plates 4,4' and an article 5 to be coated were immersed, with the anode plates 4, 4' connected to the anode of a DC power supply 7 by means of a lead wire 6 and the article 5 to the cathode of the power supply via a contact 8. In the present example, the anodes were used as a bare electrode construction illustrated in Figure 1 and as a diaphragmed electrode construction. Specifically, the latter construction was obtained by setting up a diaphragm box 9 round the anode plate 4', disposing an ion-exchange resin membrane 10 in the plane of the diaphragm box 9 intervening between the anode plate 4' and the article 5 under treatment, and filling a diaphragm water 12 in the box 9. If the anode is formed in such a diaphragm-electrode construction as described above, the coat of electrodeposited is produced

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with improved quality because even if the material of the anode dissolves out slightly from the anode, the dissolved material is prevented from mingling into the paint solution.

Figure 3 illustrates the location of anodes in the longitudinal direction of an electrodepositing cell. In the figure, 4 denotes an anode in a bare construction and 4' an anode in a diaphragm-electrode construction.

Electrodeposition coating was carried out by the following procedure described in Example 1 (B) under the conditions described similarly.

As materials for the anodes in this example, there were used stainless steel (SUS 316), carbon (graphite) and ferrite D.

The anodes made of these materials were operated for electrodeposition coating for a period of about one year. The weight reduction of each anode plate was measured. The results were as shown in Table 3. It is noted from this table that the anodes using ferrite suffered the least loss of weight. As regards the quality of coat of electrodeposit, while the coat produced by using the ferrite anodes posed no noticeable problem, that produced by using stainless steel anodes was found to have an increased Fe ion content and showed a rather coarse skin. In the case of the coat produced by using anodes of carbon, a part of carbon fell off and the paint solution was consequently found to contain finely divided particles of carbon, with the result that the produced coat suffered from a poor appearance.

Table 3

Material of anode	Reduction in thickness (mm/year)
Ferrite	Less than 0.1
Carbon	1.0
Stainless steel (SUS 316)	3.0

From the foregoing description, it is clear that the cationic electrodeposition coating involved in this example entailed virtually no dissolution of the electrode during the electrodeposition because the anode plates were formed by using a sintered mass of metal oxide excelling in electro-

conductivity and that, consequently, there was no possibility that ions as impurity would mingle into the paint solution. Since the anodes were not oxidized by the oxygen generated near the anodes during the electro-deposition, there was no possibility that the anodes would be degraded
5 by oxidation or partially separated off. Thus, the paint solution was free from adulteration with impure fine particles and the formed coat acquired a smooth, flawless skin. Furthermore, since the anodes were not degraded, they enjoyed increased durability, obviated the necessity for replacement, and acquired a merit of economizing both cost and labor.

10 Now, a typical concrete construction of the anodes of this invention will be described.

EXAMPLE 4.

Figure 4 and Figure 5 represent an electrode according to the present invention. A bar of stainless steel 11a was provided at the upper end
15 thereof with a terminal 1a. The shank of this stainless steel bar 11a was covered with a tube 4a of sintered mass of metal oxide closed at the lower end and having a U-shaped cross section, through an electroconductive material 13 such as lead, solder and electroconductive adhesive. In this electrode, since the sintered mass of metal oxide 4a was electrically
20 connected over the entire inner wall surface thereof to the bar of stainless steel 11a through the electroconductive material 13, neither rise of temperature nor loss of uniformity of current distribution occurred when a large electric current is flown. Further owing to the characteristics of stainless steel, there is no possibility that the sintered mass 4a would shed metal
25 ions even if the sintered mass is broken to consequently make the stainless steel bar 11a exposed.

The cationic electrodeposition coating using the electrodes formed in the aforementioned construction with ferrite as a sintered mass of metal oxide (hereinafter referred to as "ferrite electrodes") is satisfactorily
30 carried out similarly to those of Examples 1 through 3 as illustrated in Figure 1 or Figure 2.

The foregoing coating operation by cationic electrodeposition was carried out using Power-top U-30 (a paint produced by Nippon Paint Co., Ltd) as a paint under a DC voltage of 250 to 280 V, with the length of the
35 electrodes fixed at about 1800 mm, to coat about 15,000 automobile bodies as articles to be coated per month of steel plate of about 50m^2 for a total period of about one year. It was observed that both the ferrite

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electrodes used in the bare construction and those used as enclosed with the diaphragm box 9 showed only a very small loss of weight to such an extent that their diameters decreased from 28mm to about 27.5mm. Thus, it was found that the electrodes could still be in service. Further, the electric current from the electrodes was found to flow uniformly through the entire surface of ferrite bars and the electrodes themselves little generated heat and entailed no particular problem.

For the purpose of comparison, the coating operation following the procedure of Example 4 was repeated by using other electrodes. Consequently, the following results were obtained.

- 1) When the electrodeposition coating was carried out by using ferrite electrodes which each comprised a sintered metal oxide tube 41 of ferrite with a terminal 12 attached to the upper end thereof through an electroconductive material 14 as illustrated in Figure 6, heat generation occurred where the sintered tube 41 and the terminal 12 were joined and the current distribution was different between the terminal side and the free end side of the sintered tube 41. There was only a small flow of current at the free end side. The reduction in the outside diameter after about one year service was somewhat larger on the terminal side; the diameter decreased from 28mm to about 26mm.
- 2) When the electrodeposition coating was performed by using ferrite electrodes which each comprised a sintered metal oxide plate 42 of ferrite with a terminal 12 attached to the upper end thereof through a joint 15 as illustrated in figure 7, heat generation similarly occurred where the sintered plate 42 and the terminal 12 were joined and the current distribution was different between the terminal side and the free end side of the sintered plate 42. There was only a small flow of current at the free end side. The reduction in the wall thickness after about one year service was somewhat larger on the terminal side; the thickness decreased from 5mm to about 4mm.
- 3) When the electrodeposition coating was similarly effected by using together stainless steel SUS 316 and ferrite electrodes of this invention as illustrated in figure 4 as anodes, the flow of electric current was substantially uniform and heat generation by the electrodes themselves was slight. However the reduction in outside diameter of

the electrodes after about one year service was very large such that the diameter decreased from 16mm to about 3mm. Some of the electrodes even sustained fracture due to heavy decrease in the diameter.

- 4) When the electrodeposition coating was similarly carried out by using stainless steel SUS 316 as all anodes, the electrodes sustained similarly fracture as in the case (3) above.

The paint solution contained iron ions to such an extent as to induce partial coagulation of paint. The produced coat developed a coarse skin, such as an uneven appearance and exhibited inferior anti-corrosiveness.

- 5) When the electrodeposition coating was similarly carried out by using together, as anodes, iron SS 41 and ferrite electrodes of this invention constructed as illustrated in Figure 4, the iron anode dissolved out and fractured in several days of service.

- 6) When the electrodeposition coating was similarly carried out by using together, as anodes, copper, and aluminum, and ferrite electrodes of this invention constructed as illustrated in Figure 4, the anodes of copper and aluminum dissolved out so much as to sustain fracture in several days of service.

As described above, the ferrite electrode illustrated in Figures 4-5 suffers no increase of temperature even if a large volume of electric current is flowed, and provides uniform distribution of electric current because this electrode is formed by using a stainless steel as core and covering the outer periphery of this core successively with an electro-conductive material and a sintered mass of metal oxide.

Since this electrode uses stainless steel as its metal core, the characteristics of stainless steel prevent the metal core from being appreciably dissolved out even if the sintered mass of metal oxide sustains cracks due to external impacts, for example, and this electrode is free from a coarse skin of the coat which may occur by the dissolution of copper ions or aluminum ions into the paint or the inferior anti-corrosiveness, in the case where the electrode uses copper or aluminum as the metal core.

EXAMPLE 5:

This example shows an electrode formed by joining end to end of tubes made of sintered mass of metal oxide.

Figure 8 represents this electrode in its entirety. Figure 9 represents the essential part of this electrode.

A bar-shaped metal member 11 is made of copper, iron, or stainless steel. The outer periphery of one end of this metal member 11 is covered, through an electroconductive member 13 such as of lead, solder, or electroconductive adhesive, with a sintered mass of metal oxide 4a with one end thereof closed having a U-shaped cross section and a tube of sintered mass of metal oxide 4b spaced with each other. Round the opposed portions of the upper and lower sintered masses 4a, 4b, there is provided a connecting member 16 made of resin in the shape of a sheath.

This connecting member 16 comprises of a tubular member 17 made of rigid resin such as fluorine resin (such as a resin marketed under trademark "Teflon"), polyvinyl chloride or nylon covering the outer peripheries of the opposed portions of the sintered masses 4a, 4b, O-rings 18 of Teflon, leather or rubber inserted round stepped portions 17a, 17a being formed at opposite positions on the inner wall of the tubular member 17 and interposed between said member 17 and the sintered mass of metal oxide and ringed member 19, 19 of rigid resin, such as Teflon or polyvinyl chloride, having on the outer peripheries thereof with male threads 19a, 19a to be screwed to the female threads 17b, 17b formed round the opposite edges of the inside of the tubular member 17. Because of the screw attachment of the rigid resin members 19, 19, the O rings 18 have their leading end pressed down to establish tight contact between the rigid resin member 17 and the sintered masses 4a, 4b. After the connecting member has been formed in the construction described above, liquid hardenable resin such as, for example, two-pack hardenable type epoxy resin, polyester resin, or polyvinyl chloride sol which possesses hardenability is inserted into a void space formed between the sintered masses of metal oxide 4a, 4b and the rigid resin members 19, 19 and is caused to harden at a room temperature or an elevated temperature. The liquid resin 20 is inserted in the empty space defined by the opposed edge surfaces of the sintered masses 4a, 4b, the outer periphery of the metal member 11, and the rigid resin member 17 before the screwing of the rigid resin members 19, 19. This resin 20 may be anything so long as it does not dissolve into the paint.

Owing to such a coverage structure with the resin, all the voids round the connecting member 16 are filled up, so that no paint solution is allowed to enter into the interior of the connecting member. The resin itself is not dissolved out into the paint solution. The connecting member 16 enjoys

ample strength for bending etc because the adhesive strength of the hardenable resin 20 and the mechanical strength of the rigid resin members 17, 19, 19 are added.

Electrodes of the construction described above using ferrite or magnetite tubes as the sintered masses of metal oxide were used as anodes continuously for two years in the coating by cationic electrodeposition under the same conditions as in Example 4. Then, the electrodes were examined. But, no abnormality was found in the connecting members. The electrodeposited coats produced were normal and acceptable.

10 The joining construction of two electrodes contemplated by this invention is applicable not only to the electrodes for cationic electrodeposition but also to those for other than electrodeposition.

EXAMPLE 6.

This example illustrates the construction of joining an electrode with
15 a lead wire. Figure 10 represents a side view of the electrode and Figure 11 does a cross section of the essential part thereof.

A reference numeral 4 is an electrode in which the outer circumference of a bar-shaped metal member 11 of copper, iron, stainless steel or the like as a core is covered with an electroconductive material 13 such as
20 lead, solder, or an electroconductive adhesive, and sintered mass 4a of metal oxide. To the upper end of the electrode, a sheathed lead wire 22 such as, for example, a 600-V cable having a vinyl sheath insulated with crosslinked polyethylene or a vinyl sheath insulated with vinyl is connected through a connecting part 21.

25 The aforementioned connecting member 21 will be described more specifically. The metal member 11 is provided at the upper end thereof with a male thread 11a, to which a pressure connector 24 for connecting the lead wire is fastened by nuts 23, 23. To the pressing portion 24a of the pressure connector 24, a conductor 26 such as, for example, stranded copper wire
30 of the lead wire 22 exposed by the removal of a sheath 25 is attached under pressure such as by caulking. Thus, the electrode 4 and the sheathed lead wire 22 are connected to each other.

A tubular rigid resin member 27 made of Teflon, polyvinyl chloride or the like is mounted round the outer peripheries of the electrode 4 and the
35 sheathed lead wire 22 bridging them. On the electrode 4 side of the tubular rigid resin member 27, an O ring 28 such as of Teflon, leather, rubber or the like is inserted round a stepped portion 27 formed on the inside of the member 27 while held in contact with the outer periphery of the

sintered mass 4a of metal oxide. At the same time, a rigid resin member 29 formed of Teflon or polyvinyl chloride in the shape of a hollow cap and provided on the outer periphery thereof with a male thread 29a is screwed to a female thread 27b formed at the edge on the inside. By the screwing of this rigid resin member 29, the O rings 28 are pressed by its tip to establish tight contact between the outer rigid resin member 27 and the sintered mass 4a of metal oxide. On the sheathed lead wire 22 side, a rigid resin member 30 formed of Teflon or polyvinyl chloride in the shape of a hollow cap and provided on the outer periphery thereof with a male thread 30a is screwed to the female thread 27b formed similarly at the edge on the inside.

After the connecting member is formed in the construction described above, liquid hardenable resin 31 such as, for example, two-pack hardenable type epoxy resin, polyester resin, or polyvinyl chloride sol which has hardenability is filled into the empty space between the sintered mass 4a of metal oxide and the rigid resin members 29, 27 and into the empty space formed by the sheath 25 and the conductor 26 of the sheathed lead wire 22, the pressure connector 24, the nuts 23, the male thread 11a of the metal member 11, and the rigid resin members 30, 27 and is then caused to harden at room temperature or at an elevated temperature. This resin 31 may be anything so long as it is liquid or sol and it will not dissolve out into the paint solution after hardening.

All the voids around the connecting member 21 are filled up by the treatment with resin mentioned above. Thus, there is absolutely no possibility of internal parts being exposed directly to the solution used. High electrical insulating property and high liquid-tightness can be assured. When the connecting member 21 is immersed into the paint solution from the sheathed lead wire 22, it is only through the sintered mass 4a of metal oxide that electric current is passed to the paint solution.

For electrodes constructed as described above to be used in the coating by cationic electrodeposition coating, they are immersed in an electrodeposition cell as illustrated in Figure 12 or Figure 13.

Similarly to Example 4, Power-top U-30 (produced by Nippon Paint Co, Ltd.) was employed as paint and the electrodeposition coating was carried out under the application of a DC voltage of 250 to 300V for 3 minutes. When the article 5 subjected to coating was an automobile body, throwing power was satisfactory even on the inner surface of a box-shaped body such

as a floor member. Comparing the case where one electrode of the same construction as described above was additionally used at the bottom of the cell as illustrated in Figure 12 with the case where such an additional electrode was omitted, the coat obtained on the inner surface such as of the floor member under the same conditions had a greater thickness and better quality in the former case. For evaluation of durability of the electrodes the electrodeposition coating were continuously carried out for about one year. Upon examination of the electrode, the sintered mass 4a of metal oxide was observed to have lost volume so slightly as to pose no particular problem and the resin-treated portions at the sheathed lead wire 22 and the connecting member 21 immersed in the paint solution were not found to have developed any abnormality. Further, the paint solution showed no sign of entry of dissolved ions or other foreign matters. Every coat obtained by the treatment had highly desirable quality.

Although the working examples given above are explained with reference to electrodes for cationic electrodeposition coating, the electrodes according to the present invention are not limited thereto, but may be used for power electrodeposition coating or other forms of coating.

CLAIMS

1.- An electrode for coating by cationic electrodeposition, comprising a sintered mass of metal oxide possessing electroconductivity.

5 2.- An electrode according to Claim 1, wherein the sintered mass of metal oxide is magnetite or ferrite.

3.- An electrode according to Claim 1, wherein the sintered mass of metal oxide is in a shape of a tube with one end thereof closed having metal member inserted as a core into the cavity of said tube and secured therein by means of an electroconductive material.

0 4.- An electrode according to Claim 3, wherein the metal member is a bar of stainless steel.

5 5.- An electrode according to Claim 3, wherein the tubular sintered mass of metal oxide is composed of at least two separate tubes, said metal member is inserted into and secured to the separate tubes, and a tubular rigid resin member is set round the joint portion of the separate tubes and joined therewith by use of a hardenable resin.

0 6.- An electrode according to Claim 3, wherein a sheathed lead wire is connected to the upper end of the electrode, the joint portion of the electrode and the lead wire is covered with a tubular rigid resin member, and a hardenable type of resin is filled up the cavity of said tubular rigid resin member and caused to harden for integration.

7.- A method for the coating by cationic electrodeposition, which comprises using the electrodes set forth in any of Claims 1-6 as anodes.

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Fig 1

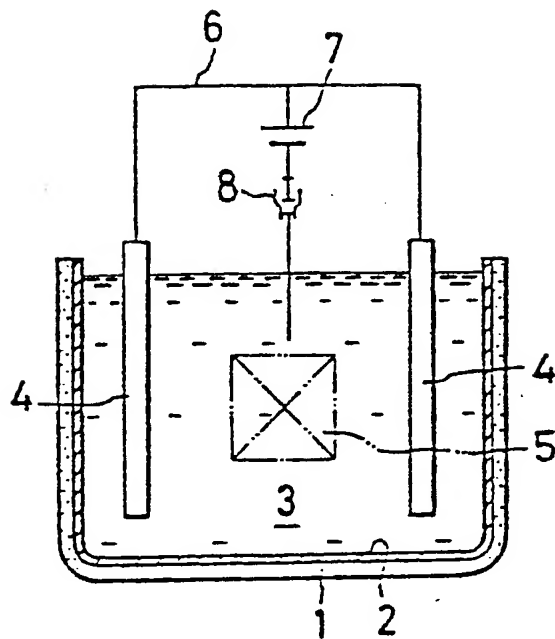


Fig 2

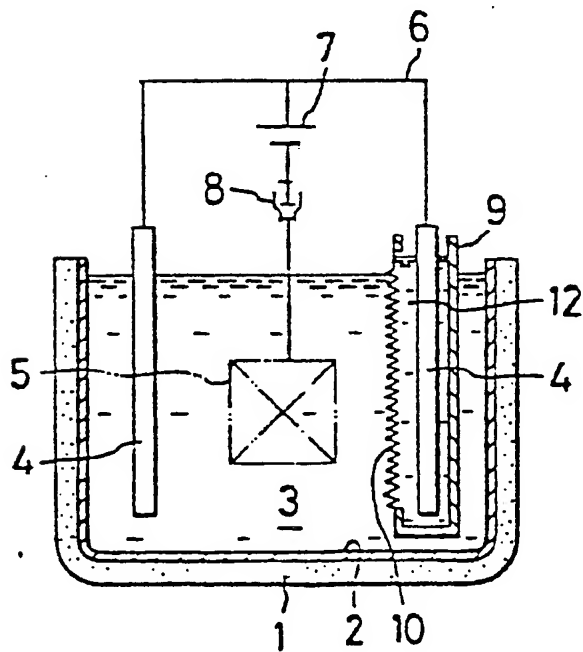


Fig 3

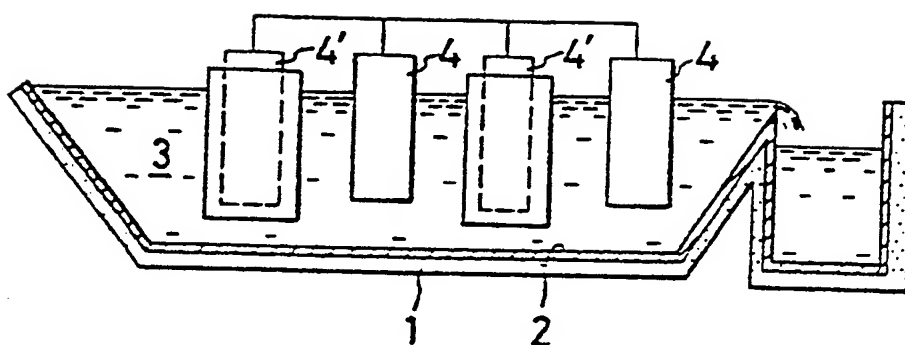


Fig 4

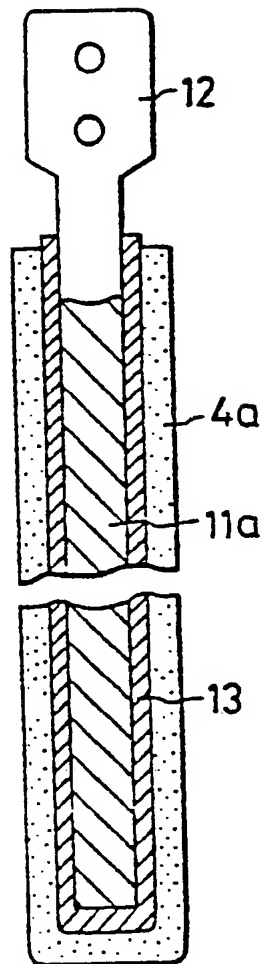
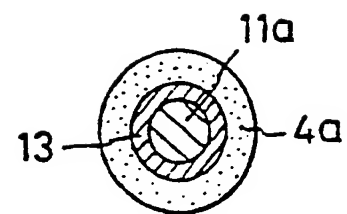


Fig 5



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Fig 6

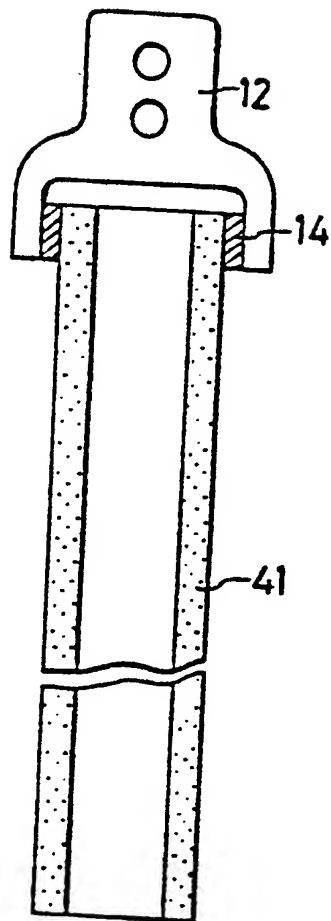


Fig 7

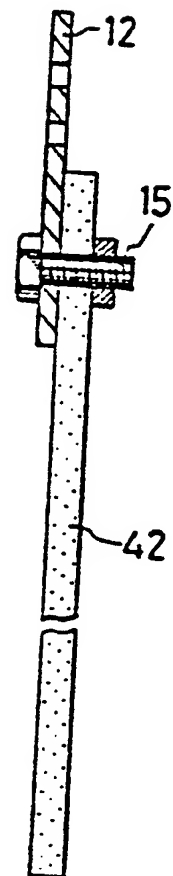


Fig 8

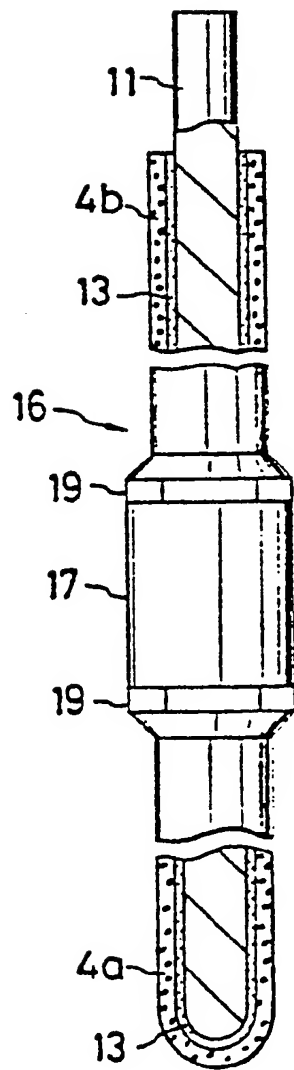


Fig 9

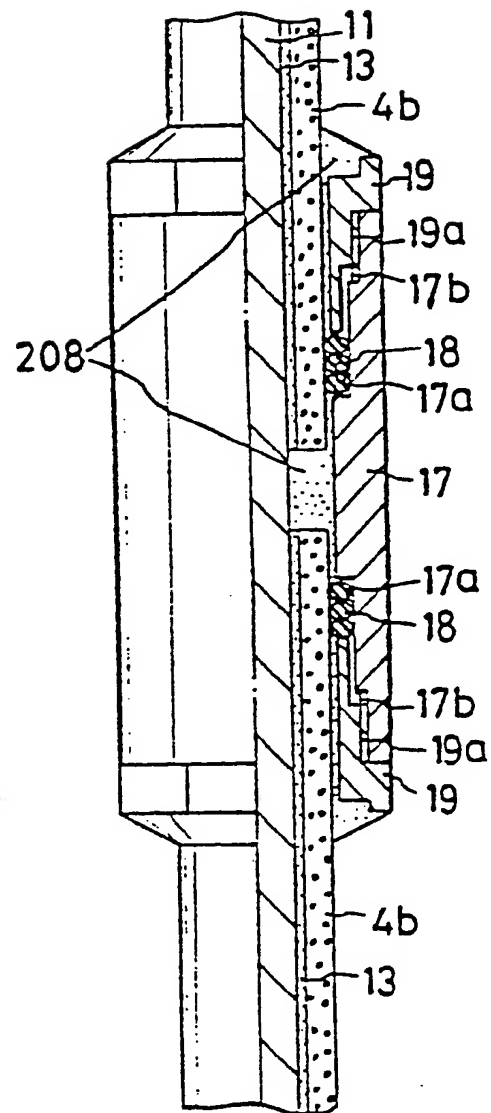
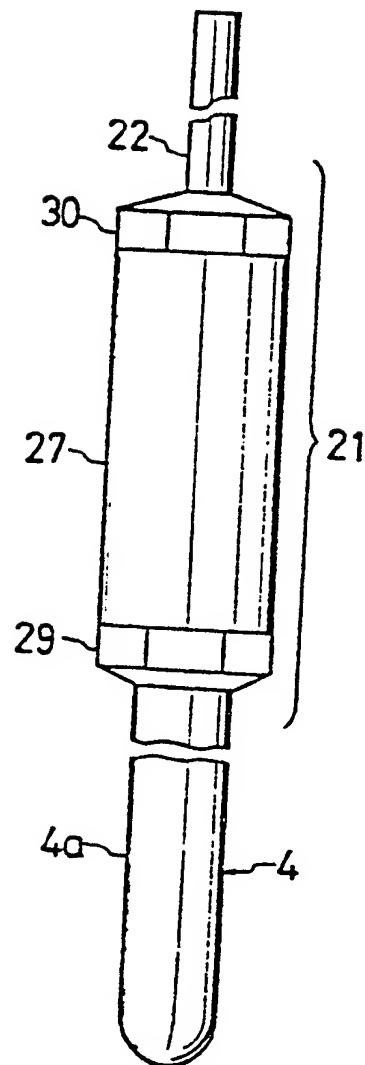


Fig. 10



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Fig. 11

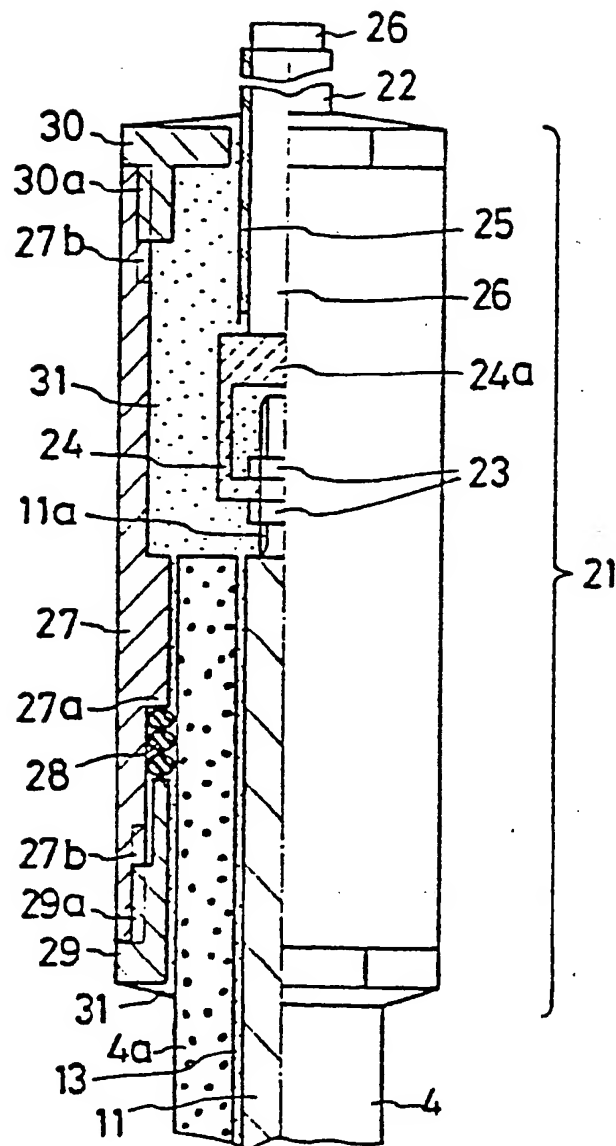


Fig 12

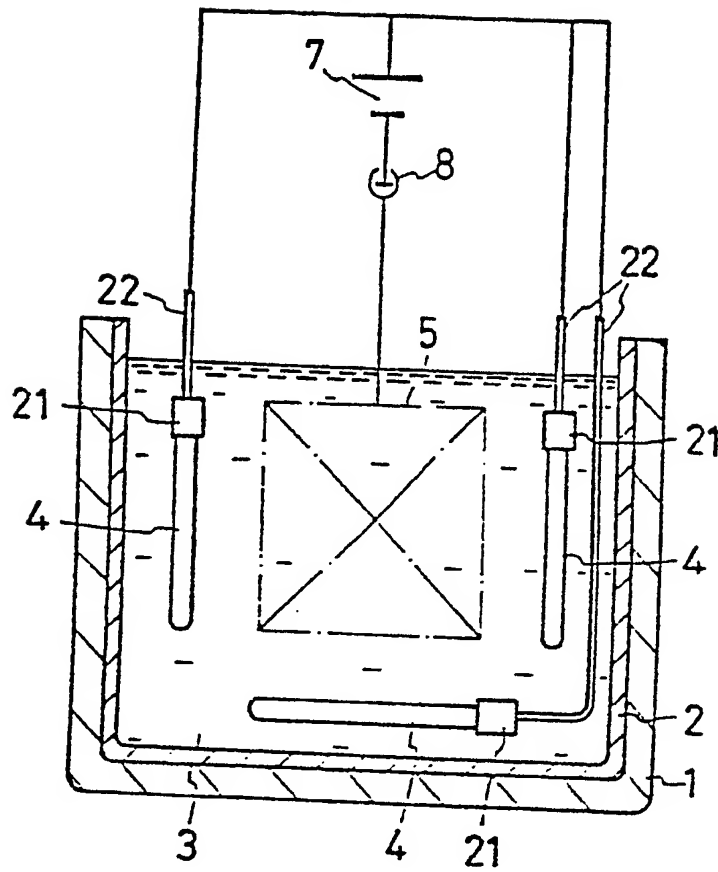
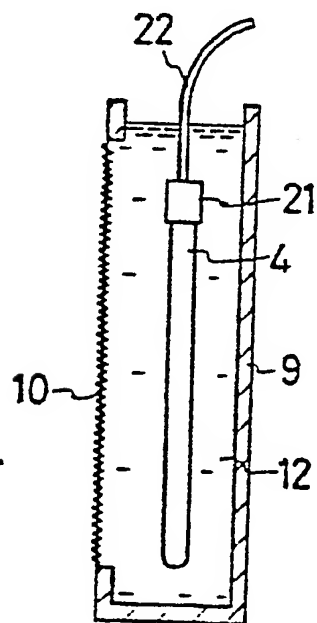


Fig 13



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INTERNATIONAL SEARCH REPORT

International Application No. PCT/JP 82/00306

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl ³ C25D 13/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
IPC	C25D 13/00-13/24, 17/10 - 17/14 C04B 35/26-35/38	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
Jitsuyo Shinan Koho 1926 - 1982 Kokai Jitsuyo Shinan Koho 1971 - 1982		
III. DOCUMENTS CONSIDERED TO BE RELEVANT¹⁴		
Category ¹⁵	Citation of Document ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	US, A, 4,231,854 (BASF A.G.) 4.November 1980 (4.11.80)	1, 7
Y	JP, B2, 51-35190 (TDK Electronics Co., Ltd.) 30. September.1976 (30.09.76) & FR, B1, 2,183,085 & GB, A, 1,433,805 & DE, B2, 2,320,883	1,2,7
Y	JP, B2, 51-35394 (TDK Electronics Co., Ltd.) 1.October.1976 (01.10.76) & FR, B1, 2,183,085 & GB, A, 1,433,805 & DE, B2, 2,320,883	1,2,7
Y	JP, B2, 51-35395 (TDK Electronics Co., Ltd.) 1. October.1976 (01.10.76) & FR, B1, 2,183,085 & GB, A, 1,433,805 & DE, B2, 2,320,883	1,2,7
Y	JP, B2, 51-35396 (TDK Electronics Co., Ltd.) 1. October. 1976 (01.10.76) & FR, B1,2,183,085 & GB, A, 1,433,805 & DE, B2, 2,320,883	1,2,7
Y	JP, B2, 52-30151 (TDK Electronics Co., Ltd.) 5. August, 1977 (05.08.77)	1,2,7
Y	JP,U, 54-169125 (TDK Electronics Co., Ltd.) 29. November.1979 (29.11.79)	3,4
<p>¹ Special categories of cited documents: ¹³</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹		Date of Mailing of this International Search Report ²
October 25, 1982 (25.10.82)		November 1, 1982 (01.11.82)
International Searching Authority ¹		

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International Application No.

PCT/JP 82/00306

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y	JP, U, 53-29752 (TDK Electronics Co., Ltd.) 14. March. 1978 (14.03.78)	3,4
Y	JP, U, 53-61413 (TDK Electronics Co., Ltd.) 25. May. 1978 (25.05.78)	5
Y	JP, U, 54-106223 (Fuji Denki Kagaku Kabushiki Kaisha) 26. July. 1979 (26.07.79)	6

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers..... because they relate to subject matter¹³ not required to be searched by this Authority, namely:2. ☐ Claim numbers..... because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out¹⁴, specifically:VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING¹⁵

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

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